Recoverable chiral sulfoxide: remote asymmetric induction in Lewis acid-promoted Diels–Alder reaction of chiral sulfinyl-substituted pyrrolyl α,β-unsaturated enones

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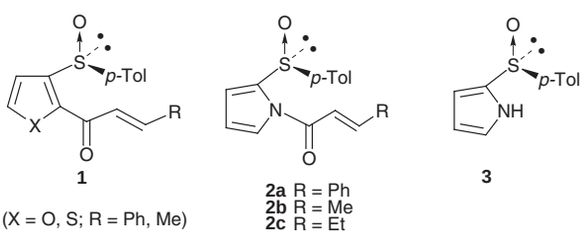
1-[2-(*p*-Tolylsulfinyl)]pyrrolyl α,β-unsaturated enones served as efficient dienophiles in the Diels–Alder reaction, where the use of aluminium chloride or a lanthanide triflate effected the cycloaddition with cyclopentadiene, affording the *endo* adduct with high diastereoselectivity. In particular, for the sulfinyl dienophile, the chiral auxiliary (*i.e.* the sulfinyl pyrrole) was recovered after use without any loss of optical purity.

Introduction

Chiral sulfoxides are useful for asymmetric carbon–carbon bond formation in organic syntheses.[1] Despite a number of these reactions using chiral sulfoxides, less progress has been made in remote asymmetric induction (=1, >3-stereocontrol). To date, some efforts have been made on dihydroxylation,[2] 1,3-allylic rearrangement,[3] reduction,[4] ring cleavage,[5] aldol condensation,[6] 1,4-conjugate addition[7] and [4+2] cycloaddition.[8] As part of our studies on remote asymmetric induction using chiral sulfoxides, we previously devised five-membered aromatic heterocycles bearing a chiral sulfinyl moiety.

The use of the furan- and thiophene-rings **1** effected highly



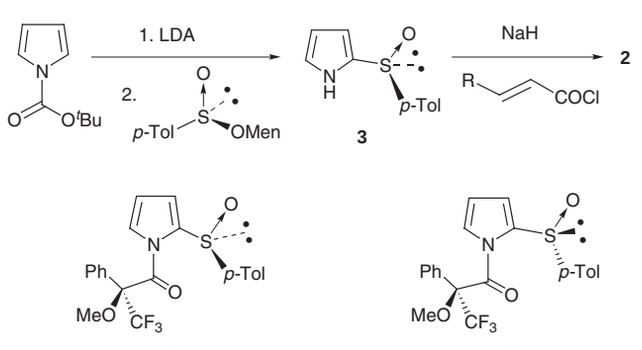
asymmetric outcomes in the Diels–Alder reaction.[8a] Encouraged by these results, we were interested in the use of a pyrrole group as a five-membered aromatic heterocycle. In contrast to the sulfoxides **1**, an important feature of the pyrrole dienophile **2** is that removal and recycling of the chiral auxiliary would be simple. Introduction of an enone functionality to the N(1) position of the sulfinylpyrrole **3** might allow easy fission of the resulting amide bond by an appropriate nucleophile such as an alkoxide at a later stage. We detail here the Lewis acid-promoted Diels–Alder reaction of sulfinyl dienophiles **2** with cyclopentadiene.[9]

Results and discussion

Preparation of sulfinyl dienophiles bearing a pyrrole ring

The pyrrole sulfoxide **2** was obtained starting with *N*-(*tert*-butoxycarbonyl)pyrrole[10] since the α-lithiation of pyrrole requires the use of a nitrogen protecting group. Although some methods for *α*-lithiation of *N*-protected pyrroles have been reported,[11] the most effective base, lithium 2,2,6,6-tetramethylpiperazide,[11a] for the lithiation is expensive. We pursued another procedure, developed by Cava *et al.*,[11b] who reported that *N*-(*tert*-butoxycarbonyl)-2-bromopyrrole is easily lithiated with *n*-BuLi, and the substitution reaction of the resulting 2-lithiopyrrole by such an electrophile as dimethyl disulfide proceeds smoothly to give the corresponding 2-substituted pyrrole in high yield. Although a similar reaction was applied to the reaction of the pyrrole **3**, it was found that racemization of the sulfinyl group took place during the reaction. A similar racemization has been observed when the reaction was carried out by the action of *n*-BuLi as a base for the lithiation of furans and thiophenes.[12] We thus turned our attention to the use of lithium diisopropylamide (LDA) as a base. Treatment of *N*-(*tert*-butoxycarbonyl)pyrrole with LDA followed by addition of (1*R*,2*S*,5*R*,S_S)-menthyl toluene-*p*-sulfinate produced **3** {mp 111–113 °C, $[a]_D^{27}$ +31.9} in 95% yield in one step. Action of the lithium salt of L-menthol generated *in situ* facilitated removal of the *tert*-butoxycarbonyl group used as an NH protecting group in the reaction media.

The high enantiomeric excess (≥99% ee) of **3** was confirmed



Scheme 1

by transformation into the Mosher's amide derivative **4** with (*R*)-(−)-α-methoxy-*α*-(trifluoromethyl)phenylacetyl chloride.[13] In the ^{1}H NMR spectrum of **4**, the MeO signal appeared at δ 3.05 as a quartet (J_{H-F} 1.7 Hz), while the diastereoisomeric amide **5**, obtained from (1*S*,2*R*,5*S*,R_S)-menthyl toluene-*p*-sulfinate, resonated at δ 3.67 for the corresponding methoxy signal. The pyrrole **3** was treated with sodium hydride and (*E*)-cinnamoyl chloride, crotonoyl chloride and (*E*)-pent-2-enoyl chloride to afford respectively **2a**, **2b** and **2c** in 93, 72 and 87% yield.

Diels–Alder reaction of 2 with cyclopentadiene

Some results of the Diels–Alder reaction of **2a** with cyclopentadiene are listed in Table 1. As can be seen in the Table, the

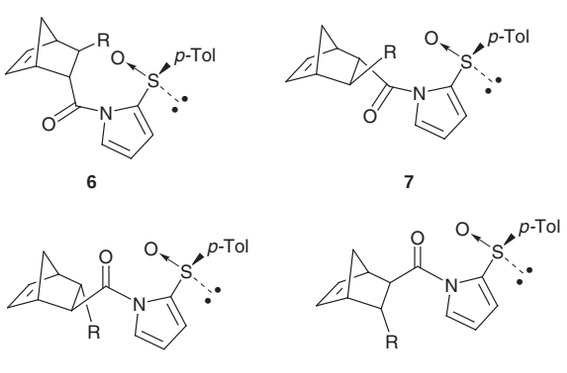
Table 1 Diels–Alder reaction of **2** with cyclopentadiene at 25 °C in CH_2Cl_2

Entry	Dienophile	Lewis acid	(equiv.)	Time (*t*/h)	Total yield (%)	*endo*/*exo*[a] (**6** + **7**)/(**8** + **9**)	De of *endo*/%[a]
1	**2a**	$BF_3{\cdot}Et_2O$	(1.0)	17	0		
2	**2a**	$ZnCl_2$	(1.0)	29	60	77/23	38
3	**2a**	$AlCl_3$	(1.0)	13	99	95/5	98
4	**2a**	$AlCl_3$	(2.0)	6	84	59/41	11
5	**2a**	$Yb(OTf)_3$	(1.0)	45	61	69/31	89
6	**2a**	$Yb(OTf)_3$	(0.2)	16	33	80/20	80
7	**2b**	$Yb(OTf)_3$	(1.0)	9	93	92/8	93
8	**2b**	$AlCl_3$	(1.0)	13	≈100	91/9	92
9	**2c**	$Yb(OTf)_3$	(1.0)	23	99	95/5	84
10	**2c**	$Sm(OTf)_3$	(1.0)	22	96	96/4	96
11	**2c**	$Nd(OTf)_3$	(1.0)	22	≈100	95/5	90

[a] Determined by ^{1}H-NMR analysis.

use of $BF_3{\cdot}Et_2O$ or $ZnCl_2$ as a promoter gave poor diastereoselectivity in the cycloaddition (entries 1 and 2). Under the conditions conducted with $AlCl_3$ or a lanthanide triflate high levels of *endo*/*exo* stereoselectivity [(**6a** + **7a**) *vs.* (**8a** + **9a**)] and diastereoselectivity of the *endo* adducts (**6a** *vs.* **7a**) were observed. With the dienophile **2a**, carrying out the reaction with a catalytic amount (0.2 equiv.) of the lanthanide triflate led to a decrease both in diastereoisomeric excess (de) and yield (entry 6). $AlCl_3$ proved to be more effective than $Yb(OTf)_3$ for increasing the yield and the diastereoselectivity, while the stoichiometric amount of the Lewis acid was needed. Increasing the amount of $AlCl_3$ (2 equiv.) gave no better selectivity. With a lanthanide triflate, the diastereoselectivities in the cycloaddition of the dienophiles **2b** and **2c** were excellent and were in the same sense as those observed for the reaction of **2a**.

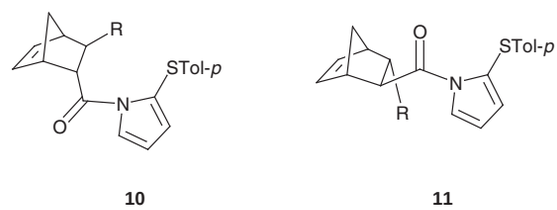
The adducts **6**–**9** obtained were inseparable from each other by column chromatography. Fortunately the major adducts **6**, obtained from a highly stereoselective reaction, were isolated purely by crystallization of the original product mixture or by preparative HPLC. The absolute stereochemistry of the major adducts **6** can be predicted in the same way from the Diels–Alder reaction described previously.[8a] It was established absolutely by transformation into the known compounds (*vide infra*).



(**a**: R = Ph; **b**: R = Me; **c**: R = Et)

An analytical sample for detection of the products **6**–**9** was prepared as follows: deoxygenation of isomerically pure **6** with $Zn/TiCl_4$[14] afforded *endo* sulfide **10**. Exposure of **10** to *m*-chloroperbenzoic acid (MCPBA) gave **6** and the enantiomer of **7** (*ent*-**7**) as roughly a 1 : 1 mixture (see Experimental section). The *endo* relationship of **6** and **7** was thus confirmed by this reaction sequence.

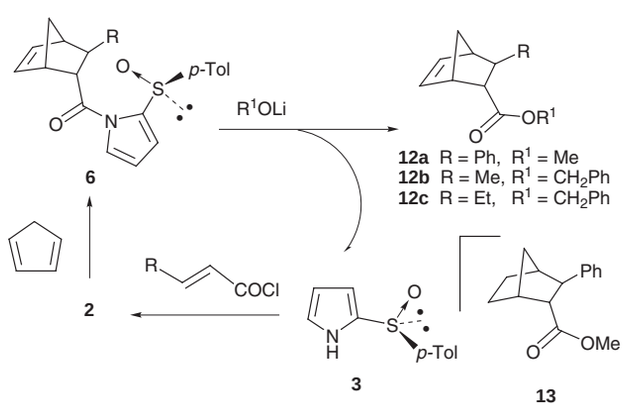
In a similar manner, the production of the *exo* adducts **8** and **9** was detected by a similar sequence by means of the sulfide **11**



10 **11**

(one enantiomer only is shown in the structural formulae, see Experimental section).

The diastereoselectivities of the *endo* adducts (**6** *vs.* **7**) were determined by the peak intensities of the olefinic signals of the adducts in the ^{1}H-NMR spectrum. The *endo*/*exo* stereoselectivities [(**6** + **7**) *vs.* (**8** + **9**)] were also estimated by ^{1}H-NMR spectroscopy. The *exo* diastereoselectivity (**8** *vs.* **9**) could not be determined because of unsatisfactory base-line separation on HPLC and NMR analysis.



Scheme 2

Finally, the absolute stereochemistry of the major adduct **6a** was determined by transformation into known compound **13**,[8a] derived by methanolysis of **6a** followed by hydrogenation of the resulting **12a** (≥97% ee). The absolute stereostructure of **6b** was also established by conversion into **12b** {$[\alpha]_D^{25}$ −122.5 (*c* 2.2, $CHCl_3$); lit.,[15] $[\alpha]_D$ −130 (*c* 2.14, $CHCl_3$)} with the known configuration. The stereochemistry of *exo* adducts **8** and **9** was not assigned.

Despite high levels of asymmetric induction in reactions using chiral sulfoxides, the chiral sulfinyl auxiliary would generally be lost at a later stage after use since the sulfinyl auxiliary is generally removed as an unstable sulfanic acid or a sulfonic acid. To date, no report concerning *direct* recovery of a chiral sulfinyl auxiliary has appeared.[16] From the viewpoint of an asymmetric reaction, the pyrrole sulfoxide **3**, the chiral source of **2**, has an advantage over the furan and thiophene derivatives **1**. The significant feature is that the sulfoxide **3**

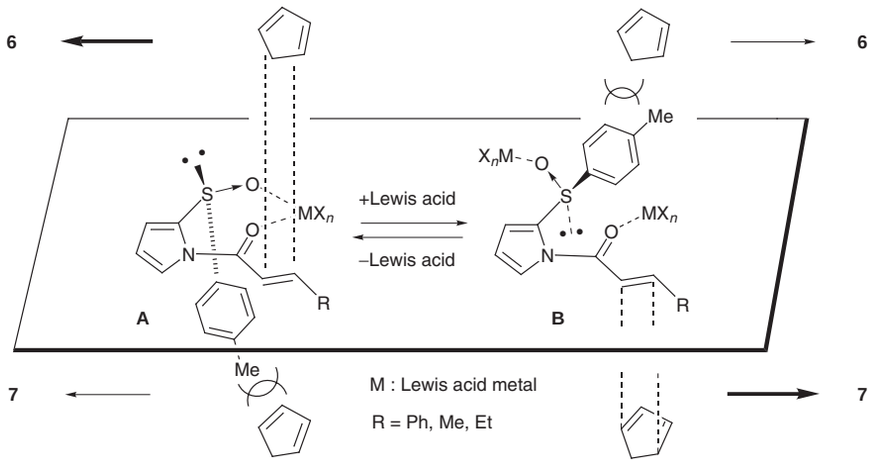


Fig. 1

is recycled after asymmetric reaction. This result is briefly exemplified by the sequence mentioned above. Treatment of adducts **6** with lithium alkoxide afforded the esters **12** in high yields, accompanied by the efficient recovery of the sulfinylpyrrole **3**. No significant loss of optical purity of **3** was observed in these reactions as determined by the Mosher's amide derivative in ^{1}H-NMR analysis.

A vast number of asymmetric, Lewis acid-catalyzed and -promoted Diels–Alder reactions have been reported;[17] nevertheless, understanding the reaction mechanism and characterization of the actual species in the Lewis acid complex are difficult. Some efforts at theoretical interpretation of the stereochemical outcome of the cycloaddition using chiral sulfoxides have been reported.[18] Although further study will be required to elucidate the stereochemical outcome of the Diels–Alder reaction, the observed excellent diastereoselectivity is consistent with our previous proposal (Fig. 1).[8a] With dienophile **2** the results can be accommodated by the cyclic transition-state model **A**, including participation by a Lewis acid, giving a favoured seven-membered complex. Cyclopentadiene should thus attack not from the sterically hindered *p*-tolyl-group side, but from the less hindered lone-paired-electron site, giving the major adducts **6a**–**c**. The decrease in diastereoselectivity using more than 1 equiv. of $AlCl_3$ (entry 4) may indicate that transition states approximated by the chelate A and the acyclic model B are competitive.

Furthermore the reasons for the high selectivity in $AlCl_3$-promoted cycloadditions are not yet clear, in spite of the fact that other typical Lewis acids such as ZnX_2 maintain only poor to moderate levels of diastereoselectivity. It is probable that the use of a lanthanide triflate as a reaction promoter would facilitate a chelating species[19] of the dienophile due to the large ion radii of the Lewis acid metal.

In conclusion, we have demonstrated that the Diels–Alder reaction of novel sulfinyl dienophiles **2** proceeds smoothly to give the adduct with high levels of *endo* selectivity and diastereoselectivity by means of a Lewis acid. The synthetic utility of sulfoxide **3** has proved to be practical because it is recycled without loss of optical purity.

Experimental

Mps were determined with a Yanaco micro melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1640 FT-IR spectrometer. NMR spectra were taken in $CDCl_3$ solution with tetramethylsilane as internal standard. ^{1}H NMR spectra were measured on a JEOL JNM-GX270 (270 MHz) or EX-400 (400 MHz) spectrometer. The following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), doublet of doublets (dd), doublet of triplets (dt), doublet of quartets (dq), multiplet (m) and broad (br). *J*-Values are in Hz. Mass spectra were taken with a JEOL JMS-D300 or JMS-SX102A spectrometer. Optical rotations were recorded on a JASCO DIP-360 digital polarimeter. $[a]_D$-Values are given in units of 10^{-1} deg cm^2 g^{-1}. Extracts were dried over anhydrous $MgSO_4$ before evaporation of solvents on a rotary evaporator under reduced pressure. Dry tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium benzophenone ketyl before use. Dry dichloromethane was distilled from CaH_2 prior to use. MCPBA was used after purification by washing with phosphate buffer of pH 7.5 according to the literature method.[20] TLC analyses were performed using Merck precoated silica $60F_{254}$ plates (0.2 mm). Column chromatography was carried out on Merck silica (70–230 mesh or 230–400 mesh). Preparative TLC was carried out with a Merck $60F_{254}$ plate (2 mm). Analytical HPLC was performed on a 5μ Develosil 60® column (4.6 × 250 mm). Preparative HPLC was carried out with a 5μ silica gel prepacked column (Kusano Kagaku). Chiral HPLC analysis was performed using a chiral column, Chiralcel OJ® (4.6 × 250 mm). Peak ratios on HPLC were determined with an integrator (Shimadzu Chromatopac C-R6A).

(S_S)-2-(*p*-Tolylsulfinyl)pyrrole 3

Butyllithium (1.57 M in hexane; 38.2 ml, 60 mmol) was added slowly to an ice-cooled solution of diisopropylamine (7.9 ml, 60 mmol) in dry THF (180 ml) under an argon atmosphere. After being stirred at the same temperature for 1.5 h, *N*-(*tert*-butoxycarbonyl)pyrrole[10] (9.87 g, 59 mmol) as a solution in dry THF (20 ml) was added to the solution at −78 °C. After being stirred for 1.5 h, a solution of (S_S)-(−)-L-menthyl toluene-*p*-sulfinate (8.8 g, 30 mmol) in dry THF (50 ml) was added. The reaction mixture was stirred at the same temperature for 17 h and quenched with saturated aq. NH_4Cl (150 ml). The organic phase was separated and the aqueous layer was extracted with EtOAc (200 ml × 3). The combined extracts were washed with saturated brine (400 ml), dried, and concentrated. The residue was purified by column chromatography on silica with hexane–EtOAc (3:1 to 1:1) to give **3** (5.82 g, 95%) as a solid; mp 111–113 °C (from EtOAc); $[a]_D^{27}$ +31.9 (*c* 2.0, $CHCl_3$); ^{1}H-NMR (270 MHz) δ 2.40 (3H, s, Me), 6.20 (1H, m, pyrrole), 6.60 (1H, m, pyrrole), 6.93 (1H, m, pyrrole), 7.28 (2H, d, *J* 8.1, Tol), 7.49 (2H, d, *J* 8.1, Tol) and 9.1–9.4 (1H, br, NH); ν_{max} ($CHCl_3$) 3410, 3180, 3000, 1490, 1080, 1020, 1010 and 810 cm^{-1}; *m*/*z* 205 (M^+), 189, 173, 157, 156, 129 and 114 (Found: C, 64.43; H, 5.39; N, 6.82. $C_{11}H_{11}NOS$ requires C, 64.36; H, 5.40; N, 6.82%). The optical purity (>99%) of **3** was confirmed by the corresponding Mosher's amide.

(*S*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA) (21 μl, 0.12 mmol) in a mixture of dimethylformamide (9 μl) and hexane (2 ml) was treated with oxalyl dichloride (51

μl, 0.58 mmol) and the mixture was stirred at room temperature for 1 h. The mixture was then filtered and the filtrate was concentrated. A mixture of **3** (20 mg, 0.1 mmol) in Et_3N (41 μl, 0.29 mmol) and 4-(dimethylamino)pyridine (4 mg, 0.03 mmol) in dichloromethane (0.5 ml) was added to the residue obtained above. The resulting mixture was stirred for 4 h and then quenched with water (5 ml). The aqueous layer was extracted with dichloromethane (5 ml × 3) and the extracts were washed with brine (5 ml), dried, and concentrated. The residue was purified by preparative TLC (hexane–EtOAc, 1 : 1) to afford the MTPA amide **4** (40 mg, 93%); ^{1}H-NMR (400 MHz) δ 2.36 (3H, s, Me), 3.06 (3H, q, *J* 1.7, OMe), 6.19 (1H, t, *J* 3.4, pyrrole), 7.02 (1H, dd, *J* 3.4 and 1.5, pyrrole), 7.08 (1H, dd, *J* 3.4 and 1.7, pyrrole), 7.23 (2H, d, *J* 8.2, Tol), 7.35–7.5 (5H, m, Ph) and 7.64 (2H, d, *J* 8.2, Tol).

(R_S)-2-(*p*-Tolylsulfinyl)pyrrole was also prepared from (R_S)-(+)-D-menthyl toluene-*p*-sulfinate in a similar manner, and the diastereoisomeric MTPA amide **5** was characterized: ^{1}H-NMR (400 MHz) δ 2.45 (3H, s, Me), 3.68 (3H, q, *J* 1.7, OMe), 6.24 (1H, t, *J* 3.4, pyrrole), 7.11 (1H, dd, *J* 3.4 and 1.8, pyrrole), 7.21 (1H, dd, *J* 3.4 and 1.8, pyrrole), 7.29 (2H, d, *J* 8.2, Tol), 6.8–7.35 (5H, m, Ph) and 7.61 (2H, d, *J* 8.2, Tol).

In the ^{1}H-NMR spectrum of the Mosher's amide **4**, two of the pyrrole protons resonated at δ 7.02 and 7.08, while those of the Mosher's amide **5** showed the corresponding signals at δ 7.11 and 7.21.

(S_S)-*N*-(*E*)-Cinnamoyl-2-(*p*-tolylsulfinyl)pyrrole 2a

Sulfinylpyrrole **3** (1.00 g, 4.9 mmol) as a solution in dry THF (10 ml) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil; 200 mg, 5.0 mmol) in dry THF (30 ml). The mixture was stirred at room temperature for 0.5 h and then (*E*)-cinnamoyl chloride (833 mg, 5.0 mmol) in dry THF (10 ml) was added to the mixture. After being stirred for 1.5 h, the mixture was quenched with water (15 ml) and the aqueous layer was extracted with EtOAc (15 ml × 3). The combined extracts were washed with brine (30 ml), dried, and concentrated. The residue was purified by column chromatography on silica with hexane–EtOAc (3 : 2 to 1 : 1) to give **2a** (1.52 g, 93%), which was recrystallized from Et_2O. Compound **2a** had mp 131–133 °C; $[a]_D^{26}$ −294.6 (*c* 1.0, $CHCl_3$); ^{1}H-NMR (270 MHz) δ 2.35 (3H, s, Me), 6.50 (1H, t, *J* 3.4, pyrrole), 7.06 (1H, d, *J* 15.5, CH=), 7.13 (1H, dd, *J* 3.4 and 1.7, pyrrole), 7.25 (2H, d, *J* 8.1, Tol), 7.41–7.60 (6H, m, Ph + pyrrole), 7.65 (2H, d, *J* 8.1, Tol) and 7.89 (1H, d, *J* 15.5, CH=); ν_{max}($CHCl_3$) 3400, 3010, 1680, 1620, 1340, 1245, 1025 and 970 cm^{-1}; *m*/*z* 335 (M^+), 319, 287, 221, 188, 157 and 131 (Found: C, 71.34; H, 5.13; N, 4.16. $C_{20}H_{17}NO_2S$ requires C, 71.62; H, 5.11; N, 4.18%).

(S_S)-*N*-Crotonoyl-2-(*p*-tolylsulfinyl)pyrrole 2b

Crotonamide **2b** was obtained in 72% yield in a manner similar to the procedure for **2a**. Compound **2b** had mp 130–132 °C (from hexane–EtOAc); $[a]_D^{25}$ −253.6 (*c* 1.0, $CHCl_3$); ^{1}H-NMR (270 MHz) δ: 1.99 (3H, dd, *J* 6.8 and 2.0, Me), 2.36 (3H, s, Me), 6.46 (1H, t, *J* 3.4, pyrrole), 6.48 (1H, dq, *J* 16.5 and 2.0, CH=), 7.09 (1H, dd, *J* 3.4 and 2.0, pyrrole), 7.21 (1H, dq, *J* 16.5 and 6.8, CH=), 7.23 (2H, d, *J* 8.3, Tol), 7.31 (1H, dd, *J* 3.4 and 2.0, pyrrole) and 7.64 (2H, d, *J* 8.3, Tol); ν_{max}($CHCl_3$) 3000, 1695, 1645, 1445, 1345, 1305, 1260, 1110 and 1030 cm^{-1}; *m*/*z* 273 (M^+), 257, 225, 188, 157, 131 and 69 (Found: C, 65.76; H, 5.59; N, 5.18. $C_{15}H_{15}NO_2S$ requires C, 65.91; H, 5.53; N, 5.12%).

(S_S)-*N*-[(*E*)-Pent-2-enoyl]-2-(*p*-tolylsulfinyl)pyrrole 2c

87% yield; mp 153–154 °C (from hexane–EtOAc); $[a]_D^{20}$ −255 (*c* 1.1, $CHCl_3$); ^{1}H-NMR (400 MHz) δ 1.11 (3H, t, *J* 7.3, Me), 2.35 (2H, m, CH_2), 2.36 (3H, s, Me), 6.43 (1H, dt, *J* 15.4 and 1.5, CH=), 6.46 (1H, t, *J* 3.3, pyrrole), 7.09 (1H, dd, *J* 3.3 and 1.5, pyrrole), 7.23 (2H, d, *J* 8.2, Tol), 7.28 (1H, dt, *J* 15.4 and 6.6, CH=), 7.32 (1H, dd, *J* 3.3 and 1.5, pyrrole) and 7.65 (2H, d, *J* 8.2, Tol); ν_{max}($CHCl_3$) 3019, 1697, 1639, 1446, 1351, 1294, 1213 and 1035 cm^{-1} (Found: C, 66.64; H, 5.96; N, 4.80. $C_{16}H_{17}NO_2S$ requires C, 66.87; H, 5.96; N, 4.87%).

Typical procedure for the Diels–Alder reaction of 2 with cyclopentadiene (entry 3 in Table 1)

Freshly sublimed $AlCl_3$ (133 mg, 1 mmol) was added in one portion to a solution of enone **2a** (335 mg, 1 mmol) in dry dichloromethane (25 ml). Freshly distilled cyclopentadiene (2.1 ml, 25 mmol) was then added to the solution and the mixture was stirred for 13 h before being treated with saturated aq. NH_4Cl (10 ml), and the organic layer was separated. The aqueous layer was extracted with dichloromethane (15 ml × 2). The combined extracts were washed successively with 3% HCl (15 ml) and brine (15 ml), dried, and concentrated. The residue was purified by column chromatography on silica with hexane–EtOAc (9 : 1 to 1 : 1) to furnish a mixture of products **6a–9a** (396 mg, 99%).

The major *endo* adducts **6a**, **6b** and **6c** were isolated in pure form by preparative HPLC (hexane–EtOAc, 7 : 1) or by crystallization of the product mixture which solidified upon storage in a refrigerator. Isolation of isomerically pure **7**, **8** and **9** was difficult by chromatographic separation.

In order to determine the product ratio, four possible analytical samples for **6**–**9** were prepared by the following sequence. Treatment of the isomerically pure **6** with Zn–$TiCl_4$ afforded a sulfide **10**. Upon exposure of **10** to MCPBA, the sulfoxide **6** and the enantiomer of **7** (*ent*-**7**) were produced in a ratio of 1 : 1. The *endo* relationship of **6** and **7** was thus confirmed by the reaction. On the other hand treatment of the mother liquid after crystallization from an original product mixture **6**–**9** (**6** enriched) with Zn–$TiCl_4$ afforded a roughly 6 : 1 mixture of two sulfides **10** and **11**, which were easily separable by preparative TLC (hexane–EtOAc, 20 : 1, 4 developments). The minor sulfide **11** was oxidized with MCPBA to produce an equal amount of a mixture of two sulfoxides. The sulfide **11**, produced by the reduction, was assumed to be in almost racemic form because the original product should contain roughly a 1 : 1 mixture of the adducts **8** and **9**. The oxidation of (±)-**11** provided (±)-**8** and (±)-**9**; however, this is of no consequence as a sample for detection of the *exo* adducts by HPLC and NMR analyses.

Both *endo* and *exo* sulfinyl isomers were inseparable by HPLC, and the *endo* : *exo* ratio [(**6** + **7**) *vs.* (**8** + **9**)] could not be determined from the peak intensities except for (**6c** + **7c**) and (**8c** + **9c**) [hexane–EtOAc (3 : 1), flow rate 1 ml min^{-1}; retention time: **9a** t_R 37.9 min; (**7a** + **8a**) t_R 41.7 and 43.6 min; **6a** t_R 48.6 min; **9b** t_R 37.2 min; (**7b** + **8b**) t_R 44.4 min; **6b** t_R 48.2 min; (**8c** + **9c**) t_R 32.2 and 33.3 min; (**6c** + **7c**) t_R 39.7 min].

The *endo* diastereoselectivity (**6a** *vs.* **7a**) was determined by the integral value of each of the olefinic signals (δ 4.98 and 6.27 for **6a** and δ 6.02 and 6.49 for **7a**) in the 400 MHz ^{1}H-NMR spectrum. The *endo* : *exo* ratio was also estimated by comparison of these signals (δ 4.98 and 6.02) with the integral value of the olefinic signals of **8a** and **9a** (δ 6.1–6.2 and 6.3–6.4). The *exo* adducts **8a** and **9a** were not clearly separable in the ^{1}H-NMR spectrum, with signals at δ 6.11 and 6.13 for each of the olefinic protons.

The *endo* diastereoselectivity (**6b** *vs.* **7b**) was determined by the integral value of each of the olefinic signals (δ 4.78 for **6b** and δ 5.85 for **7b**) in the 270 MHz ^{1}H-NMR spectrum. The *endo*/*exo* stereoselectivity was calculated by its methyl signals of **6b–9b** [δ 1.15 for **6b**, 1.08 for **7b** and 0.81, 0.91 for (**8b** + **9b**), resolved as 4 doublets].

The *endo* diastereoselectivity (**6c** *vs.* **7c**) was estimated by the integral value of each of the olefinic signals (δ 4.70 and 6.11 for **6c** and δ 5.84 and 6.39 for **7c**) in the 400 MHz ^{1}H-NMR

spectrum. The *endo*/*exo* stereoselectivity of **6c–9c** was calculated by HPLC analysis.

(1*S*,2*R*,3*R*,4*R*,S_S)-2-[2-(*p*-Tolylsulfinyl)pyrrole-1-carbonyl]-3-phenylbicyclo[2.2.1]hept-5-ene 6a.† A semi-solid; $[\alpha]_D^{23}$ −360.1 (*c* 1.0, $CHCl_3$); ^{1}H-NMR (400 MHz) δ 1.55 (1H, dd, *J* 8.8 and 1.7, 7-H^a), 1.90 (1H, d, *J* 8.8, 7-H^b), 2.38 (3H, s, Me), 3.04 (1H, br s, 1- or 4-H), 3.10 (1H, br s, 4- or 1-H), 3.29 (1H, dd, *J* 4.9 and 1.7, 3-H), 3.42 (1H, dd, *J* 4.9 and 3.4, 2-H), 4.98 (1H, dd, *J* 5.6 and 2.7, 6-H), 6.27 (1H, dd, *J* 5.6 and 3.2, 5-H), 6.41 (1H, t, *J* 3.4, pyrrole), 7.11 (1H, dd, *J* 3.4 and 1.6, pyrrole), 7.18–7.33 (8H, m, Ph + Tol + pyrrole) and 7.56 (2H, d, *J* 8.3, Tol); ν_{max}($CHCl_3$) 3000, 1710, 1445, 1395, 1325, 1240, 1095 and 1025 cm^{-1}; *m*/*z* 401 (M^+), 384, 335, 189, 157 and 131; [Found: *m*/*z* 384.1419. $C_{25}H_{22}NOS$ (*M* − OH) requires *m*/*z* 384.1422]. **7a**: ^{1}H-NMR (400 MHz) δ 1.69 (1H, dd, *J* 9.0 and 1.5, 7-H^a), 1.93 (1H, d, *J* 9.0, 7-H^b), 2.38 (3H, s, Me), 3.09 (1H, br s, 1- or 4-H), 3.2–3.4 (3H, m, 4- or 1-H and 2- and 3-H), 6.02 (1H, dd, *J* 5.5 and 2.6, CH=), 6.39 (1H, t, *J* 3.5, pyrrole), 6.49 (1H, dd, *J* 5.5 and 3.3, CH=), 6.91 (1H, dd, *J* 3.5 and 1.7, pyrrole), 7.08 (1H, dd, *J* 3.5 and 1.7, pyrrole), 7.2–7.4 (7H, m, Ph + Tol) and 7.60 (2H, d, *J* 8.3, Tol). (**8a** + **9a**): ^{1}H-NMR (400 MHz) δ 1.45 and 1.78 (total 1H, each dd, *J* 8.8 and 1.6, diastereoisomeric 7-H^a), 1.62 and 1.80 (total 1H, each d, *J* 8.8, diastereoisomeric 7-H^b), 2.36 and 2.37 (total 3H, each s, diastereoisomeric Me), 2.90 and 2.93 (total 1H, each dd, *J* 5.3 and 1.2, diastereoisomeric 2-H), 3.10 (1H, br s, diastereoisomeric 1- or 4-H), 2.90 and 3.20 (total 1H, each br s, 4- or 1-H), 3.49 and 3.75 (total 1H, each dd, *J* 5.3 and 3.4, diastereoisomeric 3-H), 6.11 and 6.26 (total 1H, each dd, *J* 5.5 and 2.7, CH=), 6.14 and 6.35 (total 1H, each dd, *J* 5.5 and 3.2, CH=), 6.28 and 6.29 (total 1H, each t, *J* 3.3, diastereoisomeric pyrrole), 7.03 and 7.04 (total 1H, dd, *J* 3.3 and 1.7, diastereoisomeric pyrrole), 7.15–7.35 (8H, m, Ph + Tol + pyrrole) and 7.57 and 7.62 (total 2H, each d, *J* 8.2, diastereoisomeric Tol).

(1*S*,2*S*,3*R*,4*R*,S_S)-2-[2-(*p*-Tolylsulfinyl)pyrrole-1-carbonyl]-3-methylbicyclo[2.2.1]hept-5-ene 6b. A crystalline solid; mp 167–169 °C (from benzene–hexane); $[\alpha]_D^{24}$ −350.4 (*c* 1, $CHCl_3$); ^{1}H-NMR (270 MHz) δ 1.15 (3H, d, *J* 6.8, Me), 1.41 (1H, dd, *J* 8.8 and 2.0, 7-H^a), 1.64 (1H, d, *J* 8.8, 7-H^b), 2.08 (1H, m, 3-H), 2.36 (3H, s, Me), 2.51 (1H, br s, 4-H), 2.84 (1H, t, *J* 3.9, 2-H), 2.96 (1H, br s, 1-H), 4.78 (1H, dd, *J* 5.8 and 3.4, CH=), 6.13 (1H, dd, *J* 5.8 and 3.4, CH=), 6.46 (1H, t, *J* 3.4, pyrrole), 7.10 (1H, dd, *J* 3.4 and 1.5, pyrrole), 7.20 (2H, d, *J* 7.8, Tol), 7.38 (1H, dd, *J* 3.4 and 1.5, pyrrole) and 7.53 (2H, d, *J* 7.8, Tol); ν_{max}($CHCl_3$) 3000, 1715, 1455, 1405, 1330, 1295, 1255, 1105 and 1035 cm^{-1}; *m*/*z* 339 (M^+), 322, 291, 189, 157 and 69 (Found: C, 71.01; H, 6.24; N, 4.05. $C_{20}H_{21}NO_2S$ requires C, 70.77; H, 6.24; N, 4.13%). **7b**: ^{1}H-NMR (270 MHz) δ 1.08 (3H, d, *J* 7.1, Me), 1.53 (1H, dd, *J* 8.8 and 1.7, 7-H^a), 1.68 (1H, d, *J* 8.8, 7-H^b), 1.95 (1H, m, 3-H), 2.35 (3H, s, Me), 2.55 (1H, br s, 1- or 4-H), 2.84 (1H, t, *J* 3.2, 2-H), 3.19 (1H, br s, 4- or 1-H), 5.85 (1H, dd, *J* 5.6 and 2.9, CH=), 6.37 (1H, dd, *J* 5.6 and 3.2, CH=), 6.45 (1H, t, *J* 3.5, pyrrole), 7.05 (1H, dd, *J* 3.5 and 1.6, pyrrole), 7.21 (2H, d, *J* 7.9, Tol), 7.39 (1H, dd, *J* 3.5 and 1.6, pyrrole) and 7.61 (2H, d, *J* 7.9, Tol). (**8b** + **9b**): ^{1}H-NMR (400 MHz) δ 0.82 and 0.91 (total 3H, each d, *J* 7.0, diastereoisomeric Me), 1.30 and 1.44 (total 1H, each dd, *J* 8.3 and 1.4, diastereoisomeric 7-H^a), 1.67 and 1.77 (total 1H, each d, *J* 8.3, diastereoisomeric 7-H^b), 2.12 and 2.14 (total 1H, each d, *J* 4.8, diastereoisomeric 2-H), 2.35 and 2.36 (total 3H, each s, diastereoisomeric Me), 2.3 and 2.6 (total 1H, m, diastereoisomeric 3-H), 2.67 and 2.72 (total 1H, each br s, diastereoisomeric 1- or 4-H), 2.75 and 2.99 (total 1H, each br s, 4- or 1-H), 6.20–6.30 (2H, m, CH=), 6.44 and 6.55 (total 1H, each t, *J* 3.5, diastereoisomeric pyrrole), 7.05–7.10 (1H, m, pyrrole), 7.20–7.30 (3H, 2 d + m, *J* 7.6, Tol + pyrrole), 7.60 and 7.62 (total 2H, each d, *J* 7.6, diastereoisomeric Tol).

(1*S*,2*S*,3*R*,4*R*,S_S)-2-[2-(*p*-Tolylsulfinyl)pyrrole-1-carbonyl]-3-ethylbicyclo[2.2.1]hept-5-ene 6c. A crystalline solid; mp 140 °C (from AcOEt); $[\alpha]_D^{20}$ −304 (*c* 1.05, $CHCl_3$); ^{1}H-NMR (400 MHz) δ 0.93 (3H, t, *J* 7.3, Me), 1.39 (1H, dd, *J* 8.8 and 1.8, 7-H^a), 1.46 (2H, quint, *J* 7.3, CH_2CH$_3$), 1.58 (1H, d, *J* 8.8, 7-H^b), 1.9 (1H, m, 3-H), 2.36 (3H, s, Me), 2.66 (1H, br s, 1- or 4-H), 2.87 (1H, t, *J* 3.8, 2-H), 2.93 (1H, br s, 4- or 1-H), 4.70 (1H, dd, *J* 5.5 and 2.8, CH=), 6.11 (1H, dd, *J* 5.5 and 3.2, CH=), 6.47 (1H, t, *J* 3.5, pyrrole), 7.13 (1H, dd, *J* 3.5 and 1.7, pyrrole), 7.21 (2H, d, *J* 8.3, Tol), 7.41 (1H, dd, *J* 3.5 and 1.7, pyrrole) and 7.54 (2H, d, *J* 8.3, Tol); ν_{max}($CHCl_3$) 2996, 1712 and 1036 cm^{-1} (Found: C, 71.18; H, 6.52; N, 3.90. $C_{21}H_{23}NO_2S$ requires C, 71.36; H, 6.56; N, 3.96%). **7c**: ^{1}H-NMR (270 MHz) δ 0.61 (3H, t, *J* 7.3 Me), 1.46 (1H, quint, *J* 7.3, CH_2CH$_3$), 1.53 (1H, dd, *J* 8.6 and 1.4, 7-H^a), 1.62 (1H, d, *J* 8.6, 7-H^b), 1.8 (1H, m, 3-H), 2.33 (3H, s, Me), 2.64 (1H, br s, 1- or 4-H), 2.81 (1H, t, *J* 3.9, 2-H), 3.18 (1H, br s, 4- or 1-H), 5.84 (1H, dd, *J* 5.5 and 2.8, CH=), 6.39 (1H, dd, *J* 5.5 and 3.2, CH=), 6.46 (1H, t, *J* 3.5, pyrrole), 7.09 (1H, dd, *J* 3.5 and 1.7, pyrrole), 7.18 (2H, d, *J* 7.8, Tol), 7.41 (1H, dd, *J* 3.5 and 1.7, pyrrole) and 7.56 (2H, d, *J* 7.8, Tol). (**8c** + **9c**): ^{1}H-NMR (400 MHz) δ 0.59 and 0.86 (total 3H, each t, *J* 7.3, diastereoisomeric Me), 1.0–1.2 (2H, m, CH_2CH$_3$), 1.23 and 1.45 (total 1H, each br d, *J* 8.6, diastereoisomeric 7-H^a), 1.31 and 1.68 (total 1H, each d, *J* 8.6, diastereoisomeric 7-H^b), 2.11 and 2.17 (total 1H, each br d, *J* 4.0, diastereoisomeric 2-H), 2.2 and 2.5 (total 1H, m, diastereoisomeric 3-H), 2.34 (3H, s, Me), 2.61 and 2.98 (total 1H, each br s, diastereoisomeric 1- or 4-H), 2.85 and 2.87 (total 1H, each br s, 4- or 1-H), 6.15–6.30 (2H, m, CH=), 6.44 (1H, t, *J* 3.5, pyrrole), 7.09 (1H, dd, *J* 3.5 and 1.7, pyrrole), 7.20 (2H, d, *J* 8.1, Tol), 7.26 (1H, dd, *J* 3.5 and 1.7, pyrrole) and 7.58 (2H, d, *J* 8.1, Tol).

Typical procedure for alcoholysis of the adduct with efficient recovery of sulfinyl auxiliary

A solution of **6b** (90 mg, 0.27 mmol) in dry THF (2 ml) was added to a solution of lithium benzylate [prepared from *n*-BuLi (1.66 M in hexane; 0.27 ml, 0.44 mmol) and benzyl alcohol (61 μl, 0.59 mmol)] in dry THF (3 ml) at 0 °C. The mixture was stirred at the same temperature for 2 h and quenched with saturated aq. NH_4Cl (3 ml). The aqueous layer was extracted with EtOAc (6 ml × 3) and the combined extracts were washed with brine (10 ml), dried, and concentrated. The residue was purified by column chromatography on silica with hexane–EtOAc (25:1 to 1:1). Early fractions contained **12b** (64 mg, 100%) as a colourless oil and the later fractions produced the sulfinylpyrrole **3** (54 mg, 99%), whose Mosher's amide showed ≥99% optical purity. Compound **12b** had $[\alpha]_D^{25}$ −122.5 (*c* 2.2, $CHCl_3$) for 94% ee by the literature value; lit.,[15] $[\alpha]_D$ −130 (*c* 2.14, $CHCl_3$).

12a: 99% yield as a colourless oil; $[\alpha]_D^{22}$ −130.2 (*c* 1.0, $CHCl_3$) for ≥97% ee; ^{1}H-NMR (270 MHz) δ 1.57 (1H, dd, *J* 8.5 and 1.7, 7-H), 1.78 (1H, d, *J* 8.5, 7-H), 3.00 (1H, dd, *J* 4.9 and 3.4, 2-H), 3.04 (1H, br s, 1-H), 3.11 (1H, dd, *J* 4.9 and 1.7, 3-H), 3.28 (1H, br s, 4-H), 3.67 (3H, s, OMe), 6.12 (1H, dd, *J* 5.6 and 2.9, 5-H), 6.42 (1H, dd, *J* 5.6 and 3.2, 6-H) and 7.15–7.35 (5H, m, Ph); ν_{max}(neat) 1730, 1325, 1255, 1195, 1110, 1015 and 700 cm^{-1}; *m*/*z* 228 (M^+), 209, 197, 163, 131 and 103; (Found: M^+, 228.1138. $C_{15}H_{16}O_2$ requires *M*, 228.1150). Compound **12a** was further transformed into known compound **13**[8a] (97% ee) through hydrogenation, and characterized by its spectroscopic and chiroptical properties.

12c: 89% yield as a colourless oil; bp 120–130 °C (bath temperature at 0.3 mmHg); $[\alpha]_D^{21}$ −115 (*c* 2.2, $CHCl_3$) for ≥95% ee as judged by chiral HPLC analysis [OJ column, 254 nm, hexane–propan-2-ol (400:1), flow rate: 0.5 ml min^{-1}; retention time: (−)-**12c**: t_R 27.0 min, (+)-**12c**: t_R 32.9 min]; ^{1}H-NMR (270

† Non-septimatic nomenclature is used in compounds **6a–6c**.

MHz) δ 0.97 (3H, t, *J* 7.3, Me), 1.4–1.6 (4H, m, 2 × CH_2), 1.70 (1H, m, 3-H), 2.47 (1H, t, *J* 4.0, 2-H), 2.61 (1H, br s, 1- or 4-H), 3.13 (1H, br s, 4- or 1-H), 5.07 (2H, AB q, *J* 12.5, $\Delta\nu$ 22 Hz, CH_2Ph), 5.94 (1H, dd, *J* 5.7 and 2.9, CH=), 6.25 (1H, dd, *J* 5.7 and 2.9, CH=) and 7.2–7.4 (5H, m, Ph); ν_{max}(neat) 2962, 1734, 1163, 1013 and 696 cm^{-1}; (Found: M^+, 256.1467. $C_{17}H_{20}O_2$ requires *M*, 256.1463. Racemic sample (±)-**12c** was prepared by the Diels–Alder reaction of benzyl (*E*)-pent-2-enoate with cyclopentadiene.

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